



**Summary of Analytical Methods, Quality Assurance,
and Quality Control for 2011 and 2012 Field Sampling
and Laboratory Water Quality Analysis**

Report 4.1.2

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December, 2013

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List of Acronyms

APHA	American Public Health Association
BOD	Biochemical oxygen demand
CBOD	Carbonaceous biochemical oxygen demand
CC	Continuing Calibration
COC	Chain of custody
Chl	Chlorophyll-a
Cl	Chloride
DOC	Dissolved organic carbon
DO	Dissolved oxygen
EC	Electrical conductivity
EERP	Ecological Engineering Research Program
ELISA	Enzyme-linked immunosorbent assay
Field Dup	Field Duplicate
HDPE	High density polyethylene
IC	Inorganic carbon
ISE	Ion selective electrode
Lab Blank	Instrument or analytical blank
Lab Dup	Laboratory duplicate
LCS	Laboratory control sample
mS/cm	MilliSiemens per centimeter
mg/L	Milligram per liter
mV	Millivolts
MS/MSD	Matrix spike and matrix spike duplicate
MSS	Mineral suspended solids
NBOD	Nitrogenous biochemical oxygen demand
NIST	National Institute of Standards and Technology
nm	Nanometers
NO ₃ -N	Dissolved nitrate plus nitrite
NTU	Nephelometric turbidity units
PC	Phycocyanin
PE Spec	Perkin Elmer Lambda 35 spectrometer
Pha	Pheophytin-a
PO ₄ -P	Dissolved phosphate as phosphorous
PT	Performance test
PTFE	Polytetrafluoroethylene
QA	Quality assurance
QC	Quality control
QAPP	Quality Assurance Project Plan
SpC	Specific Conductivity
SM	Standard Methods
SOP	Standard Operating Procedures
SWAMP	State Water Ambient Monitoring Program
SUVA	Specific ultraviolet absorbance
TAN	Total ammonium/ammonia nitrogen
TDS	Total dissolved solids
TN	Total nitrogen
TOC	Total organic carbon
TP	Total phosphorus
TSS	Total suspended solids
µg/L	Microgram per liter
UOP	University of the Pacific
VSS	Volatile suspended solids

Introduction

This report summarizes the analytical methods and results of quality assurance and control plan for the field measurement, water sample collection program, and laboratory analysis conducted by the Ecological Engineering Research Program (EERP) located at the University of the Pacific (UOP). Field measurements included chlorophyll and phycocyanin fluorescence, specific conductivity (SpC), pH, dissolved oxygen (DO), turbidity, total dissolved solids (TDS), temperature, sonde depth, and barometric pressure. Field sample collection was completed by vertically integrated water grab samples which were brought to the EERP laboratory for immediate processing. Laboratory analyses included are listed in the analytical methods section below.

The objective of this report is to describe the performance of the analytical and field crew and the quality of the data set as defined in the Quality Assurance Project Plan (QAPP) (Spier, Borglin et al. 2011). This quality assurance plan is compatible with the Surface Water Ambient Monitoring Program (SWAMP) (SWAMP, Nichol et al. 2008). For the purpose of this report, Quality Assurance (QA), as outlined in the QAPP, is the process in which the project data is evaluated and handled. Quality Control (QC) guidelines are the requirements specified in the QAPP to determine if the data is valid. The QAPP provides both a QA process and QC requirements for production of accurate and precise water quality analysis from the laboratory and the field in support of the project objectives. The QAPP imposes several layers of quality review on the data. These include procedures established for data collection and processing by the laboratory analyst and the field personnel; oversight by the QA/QC manager; review by data analysts; and review by independent personnel. This iterative process has helped create a complete and high quality data set.

Methods

Data Quality Assurance and Quality Control

Each analytical technique has established Standard Operating Procedures (SOPs) (Borglin, Burks et al. 2008) for all routine analysis methods. The SOPs ensure consistency in the analysis procedures, data reporting, and QC requirements. The SOPs were prepared by experienced analysts in collaboration with the QA/QC manager. The SOPs were kept in the analysis area and a master copy was kept on file. Daily laboratory work at the bench level is carried out according to these documents.

Data produced daily by analysts is recorded electronically and in a laboratory notebook. Electronic forms are used to enter data and for calculation of results from the unknown samples and standards using calibration parameters. Preliminary review of data quality is completed by the analyst who confirms that all standards and quality control samples meet quality control guidelines. If the guidelines are not met, the analyst confers with the QA/QC manager to identify the problem(s), and if possible samples are re-analyzed after remediation of any problems with analytical instrumentation, standards, calibration, or analysis procedures. If insufficient sample remains for re-analysis and samples did not pass QA/QC guidelines, then

results are declared invalid and not reported. Data that passed QC guidelines is then entered into the master spreadsheet.

Data in the master spreadsheet is subject to further review by applying linear regressions between correlated analyses to identify data outliers. This procedure is used to check for data entry or calculation errors. If problems are discovered during this process, the analyst is asked to recheck the data entry and quality of the sample analysis.

Quality control procedures for each laboratory analysis, discrete field sampling events, and continuous field monitoring data collection include calibration of instruments with certified standards. Quality control samples are run in conjunction with unknown samples and, depending on the analysis, could include all or some of the following: calibration check standards, laboratory control samples, sampling and analytical duplicates, matrix spikes, analytical blanks, trip blanks, and internal standards (Table 1). In addition, analyses of performance test standards are conducted at a minimum of once a year to verify the proper working order of equipment, quality of reagents, analytical technique, and analytical methods.

Sampling and Field Water Quality Measurements

Field sampling consists of collecting water samples, measuring water quality with a sonde, and recording field conditions at sites within the study area. Prior to sampling, field equipment is calibrated (see below) and trip blanks are gathered and loaded into the sampling vehicles. Chain of custody (COC) sheets are created listing the samples to be collected and disseminated to the sample crew and other pertinent individuals before sampling. Sampling is attempted for each analyte and at each site on the field sheets the day of sampling. If sample collection at a particular site is not possible, this is noted on the COC and in the field notebook. At each site, water and water quality measurements are collected. The samples are stored at 4°C after collection and returned to the laboratory for analysis.

The day before sample collection a YSI 6600 Sonde (YSI, Yellow Springs, OH) connected to a YSI 650 MDS handset is calibrated at EERP following procedures in the YSI 6-Series Environmental Monitoring Systems Handbook (Yellow Springs Instrument Co. Inc. 2002). The sonde has several probes which are calibrated independently. DO and depth are calibrated using the wet-towel method in which the sonde is placed in a tube with a wet-towel around the sensors and calibrated in a water-saturated air environment. Specific conductance, measured with a temperature compensated electrical conductivity probe (EC), is calibrated using two independent certified standard solutions (Alfa Aesar, Ward Hill, MA; and Ricca Chemical Company, Arlington, TX). Temperature calibration is checked against a National Institute of Standards and Technology (NIST) certified thermometer. The pH probe is calibrated using standards of pH 4.01, pH 7.00, and pH 10.01 (VWR International, West Chester, PA; HACH, Loveland, CO). The fluorescence probe output (for estimating chlorophyll) is recorded in Millipore water or 0 NTU water to account for drift. The turbidity probe is calibrated with two standards of 0 NTU or Millipore water and 126 NTU (YSI, Yellow Springs, OH).

Each sampling day, the sonde is recalibrated for DO at the first site to correct for ambient barometric pressure. At each sampling location, water quality data is collected for at least two

minutes using a sonde, deployed in the sample water, programmed to measure and record every parameter every four seconds to provide a statistically significant sample size ($n > 30$). The data from the sonde is also recorded in the field notebook. The parameters measured by the sonde at each site included time, temperature ($^{\circ}\text{C}$), specific conductance (mS/cm), TDS (mg/L), DO concentration (mg/L), sonde depth (ft), pH, turbidity (NTU), chlorophyll and phycocyanin fluorescence, chlorophyll content ($\mu\text{g/L}$), blue-green algae (cells/mL), and barometric pressure (mmHg).

Water samples are collected in glass 1000 mL bottles (Wheaton Science Products, Millville, NJ), 1000 mL HDPE Trace-Clean narrow mouth plastic bottles (VWR International, Radnor, PA), 250 mL HDPE Trace-Clean wide mouth plastic bottles (VWR International, Radnor, PA), 15mL HDPE centrifuge tubes (VWR International, Radnor, PA), and 40 mL trace clean vials with PTFE septa (ICChem, Rockwood, TN) in accordance with requirements for different lab analysis and volume requirements. Bottles are labeled with the appropriate sample number, site name and sampling date and rinsed with sample water prior to collection of a depth-integrated sample. River samples are collected using a telescoping pole to the end of which the sample bottle is attached. The sample bottle is rinsed with sample in the river and filled by plunging the pole up and down in the water column while the bottle fills to achieve a representative depth integrated sample. Some sites required a bucket to collect sample water because of accessibility from a high bridge or platform. For these sites, the bucket is pre-rinsed with sample water and sample bottles are filled using a rinsed funnel. Care is taken to distribute water simultaneously to all sample bottles (rather than sequentially). Samples are immediately stored at 4°C after sampling (cooler temperature is recorded in the lab upon delivery) and transported to the lab on the day of sampling. All bottle numbers, meter readings, and time in and out of the sample site are recorded in the field notebook.

For zooplankton, cyanobacteria, and microcystin analysis, samples are collected from surface water and concentrated from a 28 L bucket sampler or a 36 L Schindler Patalas Trap (Wildco, Yulee, FL) to 250 mL using a $63\ \mu\text{m}$ plankton net. After thorough mixing, concentrated samples are divided, with approximately 5 mL stored in the dark at -20°C , and analyzed in the laboratory for microcystin content using an enzyme-linked immunosorbent assay (ELISA) kit (Abraxis, Warminster, PA). The remaining concentrated sample is preserved with 1 mL Lugol's solution, 5 mL M-3 fixative (SM 10200, APHA, 2005) or a 30 mL buffered formalin sucrose mixture (SM 10200, APHA, 2005), depending on microscopic needs, and stored in amber bottles at room temperature for later identification of cyanobacteria and zooplankton by microscopy.

Post-field activities include cleaning and storing all field equipment and post-calibrating the sondes to account for drift during the sampling day. Post-calibration is completed within 24 hours of the sampling event and consists of checking sonde values to standard values. After post-calibration, sondes are cleaned and stored with a small amount of water in the calibration cup to prevent drying of the pH sensor's reference electrode.

Sample preparation and processing

Samples are received by the laboratory the same day they are sampled where they are logged into the COC sheets, inspected for damage, and stored at 4°C . Samples are analyzed, filtered, or preserved within 24 hours of collection. Archive filtrate and unfiltered samples are saved from

all sites for any needed re-analysis or additional analysis that may be determined necessary. Samples are analyzed in laboratories at EERP according to procedures described below.

Samples are collected, preserved, stored, and analyzed by methods outlined in *Standard Methods for the Analysis of Water and Wastewater*, (American Public Health Association (APHA), 2005) (SM) unless otherwise indicated. Certified standards, trace clean and certified sample bottles, reagent grade chemicals, and high purity water produced by a Milli-Q gradient system (Millipore, Billerica, MA) are used for all analyses. Glassware that is reused is cleaned thoroughly in warm water with a 1:100 solution of Alconox detergent (White Plains, NY), rinsed with 10% HCl, and rinsed a minimum of 5 times with high purity de-ionized water.

EERP Laboratory Procedures

Filters are used in the analysis of chlorophyll pigments, total suspended solids and volatile suspended solids (TSS/VSS), and an archived filter is saved for possible future analysis. Filters used for TSS/VSS analysis are pre-rinsed with high purity water (Milli-Q gradient, Millipore, Billerica, MA). All filters are pre-combusted for 4 hours at 500°C and stored in a desiccator prior to filtering. Sample bottles are shaken thoroughly before filtration and sample bottle weights are recorded before and after the samples are filtered; the difference is recorded as the filtered sample weight.

Biochemical Oxygen Demand

Unfiltered samples are analyzed for biochemical oxygen demand (BOD) by Standard Method (SM) 5210 B (APHA, 2005) with a modification for measurement of oxygen demand at ten days rather than five days. BOD samples are prepared, incubated, and measured without adding any additional microbial seed. Initial and final DO is measured using a calibrated YSI 5000 DO meter equipped with a YSI 5010 BOD probe (Yellow Springs, OH). Duplicate samples are prepared a minimum of every 20 analyses, and blanks consist of BOD buffer solution prepared according to SM 5210 B (APHA, 2005). All samples are tested at both full concentration and diluted 100 mL of sample to 200 mL of BOD buffer solution to increase the number of reportable results. All BOD tests are initiated within 24 hours of sample collection. A standard curve is prepared for each sample set consisting of a BOD standard solution (Hach, Loveland, CO) containing glucose and glutamic acid at 1, 2, 3, and 4 mg/L in dilution buffer with 5 mL of seed from a randomly selected sample. In addition, carbonaceous BOD (CBOD) is determined by adding 0.16 mg of nitrification inhibitor (N-serve, Hach, Loveland, Colorado) to a duplicate sample set. The resulting CBOD is subtracted from the total BOD to determine the nitrogenous BOD (NBOD).

Total and Dissolved Organic Carbon/Inorganic Carbon

Total organic carbon (TOC), inorganic carbon (IC), and dissolved organic carbon (DOC), are analyzed on a Teledyne-Tekmar Apollo 9000 (Mason, OH) by high temperature combustion according to SM 5310 B (APHA 2005) and quantified using a NDIR detector. TOC and IC are analyzed on unfiltered samples and DOC is analyzed from the filtrate. This machine is equipped with an auto-sampler that allows for continuous stirring of sample. Both DOC and TOC samples are preserved < pH 2 with concentrated H₃PO₄ and stored at 4°C until analysis. IC

samples are collected in the field into vials preserved with no head space, 5-10 mg CuSO₄ powder, and stored at 4 °C until analysis. Samples are analyzed within 28 days of collection.

SUVA

Specific ultraviolet absorbance (SUVA, L/mg Carbon- m) is measured on filtered samples by recording absorbance at 254 nm on a Perkin Elmer Lambda 35 spectrometer (Wellesley, MA) (PE Spec), multiplying the value by 100, and dividing the resulting value by the DOC value according to SM 5910B (APHA 2005; Potter and Wimsatt 2005).

TSS/VSS

Total suspended solids (TSS), mineral suspended solids (MSS), and volatile suspended solids (VSS) are analyzed by SM 2540 D and E (APHA 2005). Typically 1000 mL of sample is filtered on pre-weighed, pre-combusted, Whatman GF/F filters. The filters are placed in an aluminum dish and dried at 103-105 °C under vacuum to constant weight. After drying, the filter and dish are allowed to cool in a desiccator and are weighed for TSS determination. The dried and weighed filters are subsequently combusted at 550 °C for 6 hours and reweighed for MSS determination. VSS concentration is calculated by subtracting MSS from TSS.

Chlorophyll-a

Chlorophyll-a (chl) and pheophytin-a (pha) are extracted and analyzed using UV absorption as described in SM 10200 H (APHA 2005). Both the trichromatic chl and the pha methods are used for quantification. Approximately 1000 mL of sample is filtered using a vacuum filtration onto a Whatman GF/F filter within 24 hours of sample collection. The sample is kept in the dark during storage and filtration. After the water is removed, saturated MgCO₃ is applied to the sample on the filter and the filter is stored at -20 °C for up to 21 days before analysis. Extraction is performed by grinding the filter with a Teflon tissue grinder in 90% acetone-10% DI water solution saturated with MgCO₃. The extracted sample is centrifuged for 20 minutes at 2000 rpm and chl and pha are quantified by measurement of the supernatant on the PE Spec using a 5 cm path length cell.

Alkalinity

Alkalinity is measured within 24 hours of sample collection according to SM 2320B (APHA 2005) by titration of a 50 mL sample with 0.02 N H₂SO₄ to an endpoint of pH 8.3 and 4.5. Samples are stirred continuously during titration. The pH meter is calibrated before each use.

Nitrogen Species

Total ammonium/ammonia nitrogen (TAN), dissolved nitrate plus nitrite (NO₃-N), and total nitrogen (TN) are quantified using the TL-2800 ammonia analyzer (Timberline Instruments, Boulder, CO). TAN is analyzed on unfiltered samples that are frozen within 24 hours of collection. The instrument introduces a caustic solution to the sample to adjust pH to 11-13 which transforms NH₄⁺ to NH₃ (g). NH₃ (g) then diffuses through a gas permeable membrane

and dissolves in a buffer solution causing a change in conductivity which is correlated to the NH_3 concentration (Carlson 1978; Carlson 1986; Carlson, Cabrera et al. 1990). $\text{NO}_3\text{-N}$ is determined from filtered samples that are frozen within 24 hours of collection. $\text{NO}_3\text{-N}$ and $\text{NO}_2\text{-N}$ are converted to NH_3 by passing the sample through a Zn catalyst, and then is analyzed as described for the TAN sample above. Total N is quantified from digested unfiltered samples that are frozen within 24 hours of collection. To digest samples, 5.0 mL of each sample is aliquoted into trace clean 16x150 glass tubes with PTFE lined caps (VWR International). Five mL digestion reagent is then added (10 g $\text{K}_2\text{S}_2\text{O}_8$, 6 g $\text{B}(\text{OH})_3$, and 3 g NaOH in 1000mL Millipore water) followed by autoclaving in a Tuttnauer Brinkman autoclave (Westbury, NY) (Yu, et al. 1994). After cooling, TN is determined using the nitrate method as described above. The Timberline instrument automates conversion of NO_3 to NH_3 using the Zn catalyst, mixing of the caustic solution with the sample, pumping the sample across the membrane, and pumping the buffer solution through the gas permeable membrane.

Silica

Samples for dissolved silica ($\text{SiO}_4\text{-Si}$) are filtered through a pre-rinsed, 0.45 μm pore size cellulose lure-lock syringe filter (Nalgene, Rochester, NY) within 24 hours of collection and stored at 4 °C until analysis. Dissolved $\text{SiO}_2\text{-Si}$ concentration is determined using a modified Heteropoly Bluemolybdosilicate method (modified SM 4500- SiO_2 D) (APHA 2005) using Hach reagents (Loveland, CO) and measurement at both 650 nm and 815 nm.

Phosphorus

Dissolved phosphate ($\text{PO}_4\text{-P}$) is quantified in filtered samples by the ascorbic acid method (adapted from SM 4500-P-E) using Hach PhosVer3 packets (Loveland, CO) and measurement at 890 nm. One set of samples is filtered in the field within 15 minutes of collection and analyzed within 24 hours of collection. A duplicate set of samples is filtered in the laboratory within 24 hours of collection and then frozen for 28 days. The first method is recommended by SWAMP, and the second method was previously used by EERP. Duplicate samples were compared for two years and the two methods were found to be comparable (see Results section and Figure 1). Total phosphorus (TP) is determined on 5.0 mL of unfiltered sample by persulfate digestion and colorimetric determination by the ascorbic acid method (adapted from SM 4500-P B, E). To digest samples, 5.0 mL of each sample is aliquoted into trace clean 16x150 glass tubes with PTFE lined caps (VWR International). 5.0 mL digestion reagent is then added (10 g potassium persulfate, 6 g boric acid, and 3 g NaOH in 1000mL Millipore water) and samples are autoclaved in a Tuttnauer Brinkman autoclave (Westbury, NY) (Yu, et al. 1994). After digestion and sample cooling, the TP concentration is determined spectrophotometrically using Hach PhosVer3 packets (Loveland, CO) on the PE Spec (Shelton, CT).

Chloride

Chloride (Cl) is measured according to EPA method 9212 using an ion selective electrode (ISE) made by Thermo Scientific (Beverly, MA). Ion strength adjustor (Thermo Fisher Scientific, Beverly, MA) is added in a 1:50 ratio to samples before analysis. Samples are continuously

stirred during measurement and temperature is recorded. Concentration is calculated by comparing the mV reading of the probe to a logarithmic calibration curve.

Microcystin

Microcystin is measured on concentrated samples using an enzyme-linked immunosorbent assay (ELISA) kit (Abraxis, Warminster, PA). The kit comes with five calibration standards and one control. Microcystin concentration is determined at 490 nm. Concentration is inversely proportional to absorbance at 490 nm on a logarithmic scale.

Zooplankton

Zooplankton analysis follows U.S. EPA LG403. Briefly, zooplankton samples are thoroughly mixed by inversion and a 5 - 20 mL subsample is taken from each using a Stempel pipette (volume adjusted for sediment amount in sample). The subsamples are added to a settling apparatus and settled for 5 – 20 hours depending on volume. Prior to settling, 100 µL of 1% rose Bengal dye is added to facilitate counting of zooplankton. Counting is done on a Leica DMIL inverted light microscope (Wetzlar, Germany) set to 100 x magnification.

Results and Discussion

Summary of QC samples

Two major quantitative means are used to evaluate the performance of the laboratories and field crew. The first is routine measurement of QC samples and the second is an evaluation of independently prepared performance test (PT) samples. The summary of the QC samples run in conjunction with sample collection will not address the actual values or trends in the samples collected. The QC data collected addresses the precision, accuracy, and the overall confidence in the produced data set.

Laboratory QA includes all the required QC samples: calibration checks, laboratory check samples, field duplicates, matrix spikes, and blanks run in conjunction with the unknown samples.

Outside PT samples (Resource Technology Corporation Laramie, WY), (Ultra Scientific, Kingstown, RI), and (ERA, Golden, CO) are purchased for an additional assessment of the laboratory capabilities. This allows the analysts to address analysis accuracy by providing a quality check from an independent source.

In 2011, the field crew attempted to collect 204 grab samples. Of these, field measurements were collected for 195 samples, and 199 grab samples were collected for laboratory analysis, and 171 concentrated samples were collected for laboratory analysis. In 2012, the field crew attempted to collect 209 grab samples. Of these, field measurements were collected for 202 samples, 202 whole water grab samples were collected, and 192 concentrated samples were collected for laboratory analysis. Laboratory samples had an overall QC pass rate of 98.7% in

both 2011 and 2012. Field instrument calibration had an overall QC pass rate of 96.8% in 2011 and 98.9% in 2012.

After two years of collection (n=377), duplicate samples were compared to determine a relationship between the two preservation methods for dissolved PO₄-P. In one method, recommended by SWAMP, the samples were filtered in the field within 15 minutes of collection and analyzed within 24 hours. In the second method, used by EERP prior to 2010, samples were filtered in the laboratory within 24 hours of collection then frozen and analyzed 28 days later. The two methods were highly correlated ($r^2=0.965$) and no significant difference was found between the two preservation methods ($P_{\text{field filtered}}=1.000*P_{\text{lab filtered}} + 0.006$) (Figure 1).

Discussion of QC issues

A detailed summary of the 2011 laboratory QC for each analysis is provided in Table 2 and specific QC issues are discussed below.

1) Chloride (sample holding time)

In October of 2011, the chloride ion selective electrode lost its sensitivity. There was a delay in receiving the new probe after it was ordered, causing some of the samples to be analyzed past the normal 28 day holding period. Chloride is a fairly stable ion and we do expect any significant changes in the chloride samples that were held past 28 days before analysis.

2) Silica (samples lost)

The silica samples that were not analyzed were preserved incorrectly (frozen instead of refrigerated) which significantly decreases their analytical response. One set was mistakenly placed in the freezer, and a few of the samples from other sets were stored in the back of the refrigerator and had frozen there. After this occurred, all laboratory staff were reminded of this issue and samples were stored in the refrigerator door where air circulation is better.

3) TOC/DOC (sample holding time)

The instrument that measures TOC/DOC and IC had a few mechanical issues that were resolved, but resulted in some of the samples being analyzed beyond their normal holding time.

4) BOD/CBOD/NBOD (blanks not passing)

There were some issues with BOD/CBOD/NBOD blanks failing. This issue was addressed by installing a distillation unit ahead of the Millipore water filtration unit. Additionally, all but two of the BOD measurements were made on undiluted sample, so the high blank water would not have affected the BOD/COD/NBOD value of these samples. The BODs from the set of samples collected on 6/2/11 had their final reading taken two days late. This data was included in the final data set, but was clearly labeled with this problem identified.

5) Chlorophyll (deviation from standard protocol)

Two set of chlorophyll samples, analyzed together, were left out of the refrigerator, but protected from light exposure between the grinding step and the time their absorbance was read. These samples have been clearly identified in the data set as having this problem.

A detailed summary of the 2012 laboratory QC for each analysis is provided in Table 4 and specific QC issues are discussed below.

- 1) Chlorophyll (sample holding time)
The 9/27/12 set of chlorophyll samples was analyzed two weeks after its holding time; this is noted in the final data set.
- 2) Silica (sample lost)
On 5/24/12 and 7/19/12 one silica sample was lost due to a dilution error.
- 3) Inorganic carbon (sample lost)
On 5/10/12 one inorganic carbon sample froze in the refrigerator and broke its glass container and could not be analyzed.
- 4) Nitrogen (sample holding time)
One batch of ammonia and one batch of Total N samples were analyzed beyond the normal 28 day holding period; however, past results showed that frozen samples can be stored for up to a year for ammonia, nitrate, and total nitrogen analysis without any significant concentration changes.
- 5) TSS/VSS/MSS (outlier)
One TSS/VSS/MSS sample on 4/19/12 had questionable results so the data was excluded.
- 6) BOD/CBOD/NBOD (sample lost)
The BOD, CBOD and NBOD samples from 6/28/12 were lost due to the BOD incubator's compressor failing and resulting in high temperatures. The last set of samples was not analyzed for BOD, CBOD and NBOD because the final reading fell during the Christmas holiday. In the 5/31/12 and 6/13/12 sample sets, some of the BOD, CBOD, and NBOD lab buffer blanks failed. After the problem was identified, a new BOD buffer container was put in use, new concentrated BOD buffers were made, and the cleaning procedures were reviewed.
- 7) Field instrument calibration
On two occasions, the 126 NTU turbidity standard failed in pre-calibration. After talking to the manufacturer, it was discovered that these standards were made for use on a different type of instrument and were incorrectly advertised on their webpage. In 2012, no other specific issues came up with field instrument calibration, although, the post deployment QA/QC failed for Chlorophyll-a (% fluorescence) two times meaning that the post reading in milliQ water was above the 0.2 detection limit set by the manufacturer and equivalent to 1.8 µg/L chl-a. Table 5 summarizes the results of the 2012 field instrument quality control tests including pre and post calibration checks.

Results and Discussion of Performance Tests

Table 6 summarizes the 2011 results of performance test (PT) standards (Resource Technology Corporation Laramie, WY) and (Ultra Scientific, Kingstown, RI) used to independently assess laboratory performance. All samples except chloride were found to be within acceptable tolerances. Chloride was measured by two different methods, ion chromatography and ion selective electrode, which both had very similar results. For the next set of performance check standards chloride will be ordered from a different manufacturer. Because chloride is only a secondary analyte for this project, and both of our lab measurements were in agreement, a new proficiency check standard was not ordered immediately.

Table 7 summarizes the results of the 2012 PT standards (Resource Technology Corporation Laramie, WY), (Ultra Scientific, Kingstown, RI), and (ERA, Golden, CO). PT standards were analyzed on 5/31/12 and near the end of 2012 sampling on 11/29/12. The 5/31/12 PT standards had four problems.

1) Nitrate

One of the two nitrate standards came out low (73% of the expected value). This low nitrate value was determined to be a dilution error.

2) Total P

The Total P PT test also came out low (75% of the expected value). Calibration standards run in conjunction with this test were passing (80-120% of expected), but were on the low end of passing. After discussing the issue with the QA officer and double checking the calibration curve, it appeared that there may have been a problem during the digestion step in which sample/standard can be diluted if the caps do not fully seal during the autoclaving step. The analyst was instructed to be extra careful about tightening the caps before autoclaving and checking the fluid level after autoclaving to ensure sample was not contaminated in this manner in the future.

3) TSS

The TSS sample was lost by a new laboratory analyst so the sample result was never determined.

4) CBOD

The CBOD number came out higher than expected (206%). The laboratory analyst discussed this issue with the QA officer and several possible sources of error were identified and tested. A new lot of n-serve (the chemical which stops nitrification) was just opened and could have caused a problem; to address this, a new bottle was ordered for comparison. The possibility that not enough n-serve was dispensed from the container was investigated, but the dispensed amount was found to be very consistent when tested by weight. The BOD buffer container could have been contaminated, so the analyst implemented a more rigorous washing procedure between uses. The compressor in the BOD incubator broke shortly after the performance test (6/28/12) resulting in overheating of the incubator, so it is possible that the temperature was high during the

test, but there was not a continuous temperature monitor in the incubator at the time and only start and end temperatures were recorded. After this issue came up, a continuous temperature monitor was installed in the BOD incubator. The TOC and BOD both passed using the same PT standard so a dilution error was ruled out.

After identifying and addressing the possible sources of errors, each of the four failed tests were re-run on newly ordered standards on 8/9/12 and all of these PT standards passed.

Another batch of PT standards was run near the end of the year (11/29/12). All standards passed except the BOD and CBOD test. This error was linked back to another temperature problem with the BOD incubator. Using the continuous temperature data logger, it was discovered that the incubator's average temperature was 21.32°C (more than the allowable 1°C above or below the required 20°C for the test). The failed BOD standard was started on 12/17/12 after all other samples had been completed. All of the continuous temperature data was analyzed and this temperature problem started at 12:00 pm on 12/17/12 and did not affect any samples other than the PT test. After discovering the source of this error, another BOD standard was ordered and run in a different incubator on 1/30/13 and this second standard passed.

Acknowledgements

We gratefully acknowledge the Ecosystem Restoration Program and its implementing agencies (California Department of Fish and Wildlife, U.S. Fish and Wildlife Service, and the National Marine Fisheries Service) for supporting this project (E0883006, ERP-08D-SO3).

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Table 1. Definition of analytical quality control samples used in laboratory analysis.

QC Type	Definition	Frequency	Used to Evaluate	Limits	Corrective Action
Performance test standard (PT)	Certified reference standard	Per analytical method or manufacturer's specifications	Accuracy, Precision	Per manufacture's specifications	Affected samples and associated quality control must be reanalyzed following successful instrument recalibration.
Continuing Calibration (CC)	Standard solution at a concentration in the center of the calibration curve.	Every 10 samples	Accuracy, Comparability	80 -120%	Analysis cannot proceed unless CCs pass. All samples/QA after the last passing CC must be re-analyzed
Laboratory Control Sample (LCS)	Standard solution from a different vendor than that of the calibration standard spiked with compounds of interest into a clean water matrix.	Every analytical batch or 20 samples, whichever is more frequent.	Accuracy, Comparability	81 -120%	Perform instrument maintenance and prepare new standard solution if necessary. Samples and associated QA must be re-analyzed.
Matrix Spike & Matrix Spike Duplicate (MS/MSD)	Standard solution with 2-5x the concentration of ambient compounds of interest spiked into a representative sample matrix.	Every analytical batch or 20 samples, whichever is more frequent.	Accuracy, Comparability, Precision	80 -120%; Relative Percent Difference(RPD)<25% for duplicates	If LCS passes, result may reflect matrix interference and may be reported with qualification.
Instrument or Analytical Blank (Lab Blank)	Clean water matrix, free of analyte. Analyzed in same manner as samples.	Every analytical batch or 20 samples, whichever is more frequent.	Accuracy	Measured value less than MDL or RL	In some cases, target compound values may be subtracted out, in other analyses target compounds present in blank must be flagged as contamination and may not be subtracted out.
Laboratory Duplicate (Lab Dup)	Analytical duplicate	Every analytical batch or 20 samples, whichever is more frequent.	Comparability, Precision	RPD<25% (n/a if native concentration of either sample <RL	Rerun sample. If second result is not within limits, report with qualifier.
Field Duplicate (Field Dup)	Collected in separate sampling bottles, at approximately the same time	5% of total project count	Comparability, Precision	RPD<25% (n/a if native concentration of either sample <RL	Rerun sample. If second result is not within limits, report with qualifier.
Trip Blank	Clean water matrix, free of analyte. Analyzed in same manner as samples. Prepared at the start of the field day and carried with field crew during sampling	Every field sampling day	Contamination from sample bottles, sample storage	Measured value less than MDL or RL	Rerun sample. If second result is not within limits, report with qualifier and find source of contamination and correct immediately.

Table 2. Summary of laboratory quality assurance/quality control for grab samples collected in 2011.

QA/QC test	Cl (ISE)	Si	DOC	TOC	IC	TAN	TN	NO ₃ -N	TP	Alkalinity	PO ₄ -P (lab filtered)	PO ₄ -P (field filtered)
Number of samples analyzed												
Completeness % of samples collected	100.00%	94.20%	100.00%	100.00%	99.00%	100.00%	100.00%	100.00%	100.00%	100.00%	92.50%	96.00%
% of samples completed on time	85.90%	97.00%	99.00%	94.00%	92.00%	93.50%	87.70%	94.50%	99.50%	100.00%	100.00%	100.00%
CC's	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%
LCS % passing	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%
Field Dup % passing	100.00%	100.00%	100.00%	100.00%	96.00%	100.00%	100.00%	92.00%	100.00%	100.00%	100.00%	79.20%
Lab Dup % passing	100.00%	100.00%	100.00%	100.00%		100.00%	100.00%	100.00%	100.00%	100.00%	100.00%	95.80%
Lab Blanks % passing	100.00%	100.00%	96.00%	99.30%	98.00%	100.00%	100.00%	100.00%	100.00%	100.00%	94.60%	97.90%
Trip Blank % passing	96.00%	100.00%	100.00%	100.00%		100.00%	100.00%	98.00%	100.00%	100.00%	95.70%	91.70%
MS % passing	100.00%	100.00%	100.00%	100.00%		100.00%	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%
MSD % passing	100.00%	100.00%	100.00%	100.00%		96.00%	100.00%	100.00%	100.00%	100.00%	100.00%	95.80%
MSD-RSD % passing	100.00%	100.00%	100.00%	100.00%		100.00%	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%
Overall	98.40%	99.20%	99.50%	99.40%	97.50%	99.00%	98.90%	98.60%	100.00%	100.00%	98.40%	96.00%

QA/QC test	BOD	CBOD	NBOD	Absorbance @ 254nm	Ch-a SM	Pheophyton SM	Algal pigments SM	Chl-a TriChrom	Chl-b TriChrom	Chl-c TriChrom	MSS	TSS	VSS
Number of samples analyzed													
Completeness % of samples collected	97.50%	97.50%	97.50%	100.00%	99.50%	99.50%	99.50%	99.50%	99.50%	99.50%	98.50%	98.50%	98.50%
% of samples completed on time	95.50%	95.50%	95.50%	100.00%	91.00%	91.00%	91.00%	91.00%	91.00%	91.00%	100.00%	100.00%	100.00%
Field Dup % passing	100.00%	96.00%	96.00%	100.00%	96.00%	76.00%	96.00%	100.00%	96.00%	96.00%	88.00%	96.00%	92.00%
Lab Dup % passing	83.30%	91.70%	95.80%		95.80%	95.80%	100.00%	100.00%	100.00%	95.80%			
Trip Blank % passing	84.00%	92.00%	72.00%	96.00%	96.00%	100.00%	100.00%	100.00%	100.00%	100.00%	96.00%	100.00%	100.00%
Lab Blanks % passing	75.00%	75.00%	100.00%	100.00%									
seed check for BODs % passing	88.00%												
Overall	89.00%	91.30%	92.80%	99.20%	95.70%	92.50%	97.30%	98.10%	97.30%	96.50%	95.60%	98.60%	97.60%

Table 3. Summary of 2011 field instrument calibration quality assurance/quality control tests. Includes both pre- and post- field activity calibrations.

	Depth (ft)	DO %	DO (mg/L)	SpC	LCS Spc	pH 4.0	pH 7.0	pH 10.0
Pre-Deployment % passing	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%
Post-Deployment % passing	91.70%	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%

	LCS pH 4.01	LCS pH 7.0	LCS pH 10.01	Turbidity 0 NTU	Turbidity 40 NTU	Turbidity 200 NTU	Chl fluorescence	PC fluorescence
Pre-Deployment % passing	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%
Post-Deployment % passing	75.00%	80.00%	75.00%	95.70%	87.50%	91.70%	100.00%	100.00%

Table 4. Summary of laboratory quality assurance/quality control for grab samples collected in 2012.

QA/QC test	Cl (ISE)	Si	DOC	TOC	IC	TAN	TN	NO ₃ -N	TP	Alkalinity	PO ₄ -P (lab filtered)	PO ₄ -P (field filtered)
Number of samples analyzed	202	202	202	202	202	202	202	202	202	202	202	202
Completeness % of samples collected	100.00%	99.00%	100.00%	100.00%	99.50%	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%
% of samples completed on time	100.00%	100.00%	100.00%	100.00%	100.00%	95.80%	100.00%	100.00%	95.80%	100.00%	100.00%	100.00%
CC's	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%
LCS % passing	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%
Field Dup % passing	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%	87.50%	91.70%
Lab Dup % passing	100.00%	100.00%	100.00%	100.00%		100.00%	100.00%	100.00%	100.00%	100.00%	95.80%	95.80%
Lab Blanks % passing	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%
Trip Blank % passing	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%
MS % passing	100.00%	100.00%	100.00%	100.00%		100.00%	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%
MSD % passing	100.00%	100.00%	100.00%	100.00%		100.00%	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%
MSD-RSD % passing	100.00%	100.00%	100.00%	100.00%		100.00%	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%
Overall	100.00%	100.00%	100.00%	100.00%	100.00%	99.60%	100.00%	100.00%	99.60%	100.00%	98.30%	98.70%

QA/QC test	BOD	CBOD	NBOD	Absorbance @ 254nm	Ch-a SM	Pheophyton SM	Algal pigments SM	Chl-a TriChrom	Chl-b TriChrom	Chl-c TriChrom	MSS	TSS	VSS
Number of samples analyzed	194	194	194	202	202	202	202	202	202	202	202	202	202
Completeness % of samples collected	92.80%	93.30%	92.80%	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%	99.50%	99.50%	99.50%
% of samples completed on time	100.00%	100.00%	100.00%	100.00%	95.80%	95.80%	95.80%	95.80%	95.80%	95.80%	100.00%	100.00%	100.00%
Field Dup % passing	90.90%	90.90%	90.90%	100.00%	95.80%	91.70%	87.50%	95.80%	95.80%	95.80%	91.70%	95.80%	100.00%
Lab Dup % passing	95.50%	100.00%	90.90%		100.00%	100.00%	100.00%	100.00%	86.70%	86.70%			
Trip Blank % passing	90.90%	90.90%	100.00%	100.00%									
Lab Blanks % passing	100.00%	100.00%	95.50%	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%	95.80%	95.70%	100.00%
seed check for BODs % passing	82.40%												
Overall	93.70%	96.40%	95.50%	100.00%	97.80%	96.60%	95.40%	97.70%	95.40%	95.40%	95.80%	97.20%	100.00%

Table 5. Summary of 2012 field instrument calibration quality assurance/quality control tests. Includes both pre- and post- field activity calibrations.

	Depth (ft)	DO %	DO (mg/L)	SpC	LCS Spc	pH 4.0	pH 7.0	pH 10.0
Pre-Deployment % passing	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%
Post-Deployment % passing	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%

	LCS pH 4.01	LCS pH 7.0	LCS pH 10.01	Turbidity 0 NTU	Turbidity 40 NTU	Turbidity 200 NTU	Chl fluorescence	PC fluorescence
Pre-Deployment % passing	100.00%	100.00%	100.00%	100.00%	100.00%	88.9% ^a	100.00%	100.00%
Post-Deployment % passing	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%	91.7% ^b	100.00%

a. On two occasions, the 126 NTU turbidity standards failed in pre-calibration. After talking to the manufacturer, it was discovered that these standards were made for use on a different type of instrument and were incorrectly advertised on their webpage.

b. The chlorophyll failed because the base line had drifted slightly and the post reading in milliQ water was above the 0.2 detection limit set by the manufacturer and equivalent to 1.8 µg/L chl-a.

Table 6. Summary of 2011 performance test standards used to independently assess laboratory performance.

Analysis	Cat#	Lot #	Result	Certified Value	Acceptance Limits	Units	% of Expected	Pass/Fail
Turbidity	QCI-250	16313	9.1	8.58	6.48-10.7	NTU	106.06	PASS
TAN	QCI-042-1	17495	1.63	2.05	1.37-2.74	mg/L	79.33	PASS
NO₃-N	QCI-042-1	17495	3.06	3.47	2.85-4.09	mg/L	88.18	PASS
PO₄-P	QCI-042-1	17495	0.75	0.758	0.557-0.960	mg/L	99.18	PASS
Total N	QCI-42-2	15231	6.44	7.49	6.37-8.61	mg/L	85.98	PASS
Total P	QCI-42-2	15231	1.72	1.77	1.39-2.16	mg/L	97.18	PASS
pH (lab probe)	QCI-010-3	12962	5.74	5.8	5.60-6.0	pH	98.97	PASS
Alkalinity	QCI-27-12	016692/016693	34.6	33.6	27.8-39.4	mg/L	102.98	PASS
SpC	QCI-27-12	016692/016693	790	749	679-832	µS	105.47	PASS
Cl (ISE)	QCI-710	72431	46.16	37.4	33.5-42.0	mg/L	123.42	FAIL
Cl (ion chromatography)	QCI-710	72431	48.09	37.4	33.5-42.0	mg/L	128.58	FAIL
Alkalinity	QCI-710	72431	329.2	352	316-387	mg/L	93.52	PASS
SpC	QCI-710	72431	936	901	846-955	µS	103.88	PASS
IC (Bicarbonate as CO₃)	WP-11-2, PEI-261	16933	132.35-C, 662.3-CO ₃	435	174-696	mg/L	152.18	PASS
TSS	WP-11-2, PEI-080	18193	80.33	78.7	66.7-90.8	mg/L	102.07	PASS
Silica	WS11-2, PEI-227	18187	9.48	10.3	8.76-11.8	mg/L	92.04	PASS
BOD	WS11-2, PEI-233	18164	99.2	94.9	47.9-142	mg/L	104.53	PASS
CBOD	WS11-2, PEI-233	18164	92.7	81.6	36.6-127	mg/L	113.6	PASS
TOC	WS11-2, PEI-233	18164	57.45	60.2	50.99-69.8	mg/L	95.44	PASS
pH (field probe)	QCI-710	70288	9	9.11	8.91-9.31	pH	98.79	PASS

Table 7. Summary of 2012 performance test standards used to independently assess laboratory performance.

Analysis	Date	Cat#	Lot #	Result	Certified Value	Acceptance Limits	% of Expected	Pass/Fail
Turbidity	5/31/2012	QC-1081	10313	9.4	8.65	6.48-10.7	108.67	PASS
TAN	5/31/2012	QC-1166	17495	1.44	2.05	1.37-2.74	70.1	PASS
NO ₃ -N	5/31/2012	QC-1166	17495	2.58	3.5	2.85-4.09	73.71	FAIL
NO ₃ -N	5/31/2012	QC-1166	17495	3.24	3.5	2.85-4.09	92.57	PASS
PO ₄ -P	5/31/2012	QC-1166	17495	0.74	0.751	.557-.960	98	PASS
TN	5/31/2012	QC-1001	18476	7.37	7.52	5.04-9.84	97.98	PASS
TP	5/31/2012	QC-1001	18476	1.58	2.09	1.67-2.56	75.45	FAIL
pH (corning lab probe)	5/31/2012	PE 1210	20287	7.67	7.61	7.41-7.81	100.79	PASS
pH (Schoh lab probe)	5/31/2012	PE 1210	20287	7.64	7.61	7.41-7.81	100.39	PASS
Alkalinity	5/31/2012	QCI-710	77178	173.4	183	165-202	94.75	PASS
Cl (ISE)	5/31/2012	506	P203-506	69.2	62.8	53.5-72.5	110.19	PASS
Alkalinity	5/31/2012	506	P203-506	122.7	117	104-129	104.87	PASS
SpC	5/31/2012	QCI-710	77178	977	994	935-1054	98.29	PASS
pH (Sonde)	5/31/2012	QCI-710	77178	9.01	9.15	8.95-9.35	98.47	PASS
IC (Bicarbonate as CO ₃)	5/31/2012	PEI183	19213	343.3	300	236-384	114.43	PASS
Si (as SiO ₂)	5/31/2012	PEI-350	19839	17.56	18.5	15.7-21.3	94.92	PASS
BOD	5/31/2012	PEI-1388	20861	10.72	7.89	3.61-12.2	135.87	PASS
CBOD	5/31/2012	PEI-1388	20861	8.06	3.9	1.71-6.10	206.67	FAIL
TOC	5/31/2012	PEI-1388	20861	4.4	5.06	3.97-6.14	86.98	PASS
COD	5/31/2012	PEI-1388	20861	13.7	12.4	3.25-21.5	110.48	PASS
TS/VS	5/31/2012	PEI183	19213	322	320	224-416	100.54	PASS
TDS	5/31/2012	506	P203-506	442	406	309-503	108.89	PASS
TP	8/9/2012	P202-525	525	4.46	5.45	4.39-6.50	81.83	PASS
NO ₃ -N	8/9/2012	P203-505	505		15.1	12.9-16.6		
BOD	8/9/2012	516	8P204-516	40.98	32.3	21.2-42.6	126.87	PASS
CBOD	8/9/2012	516	8P204-516	29.38	27.9	20.3-38.8	105.3	PASS
TSS	8/9/2012	4032	P203-4032	51.44	51.5	44.8-54.3	99.88	PASS
Turbidity	11/29/2012	893	WP-214	9	8.81	7.08-10.5	102.16	PASS
TAN	11/29/2012	584	WP-214	4.46	4.62	3.34-5.93	96.54	PASS
NO ₃ -N	11/29/2012	584	WP-214	5.46	5.49	4.47-6.39	99.45	PASS
NO ₃ -N	11/29/2012	591	WS-196	6.82	6.8	5.78-7.82	100.29	PASS
PO ₄ -P	11/29/2012	584	WP-214	2.19	2.19	1.77-2.63	100	PASS
TN	11/29/2012	579	WP-214	3.69	3.3	2.28-4.46	111.82	PASS
TP	11/29/2012	579	WP-214	7.69	9.48	7.85-11.2	81.12	PASS ^a
Alkalinity	11/29/2012	591	WS-196	181.8	175	158-192	103.89	PASS
Cl (ISE)	11/29/2012	591	WS-196	99.1	109	92.6-125	90.92	PASS
SpC	11/29/2012	591	WS-196	1132	1140	1030-1250	99.3	PASS
pH (Sonde)	11/29/2012	577	WP-214	5.95	5.93	5.73-6.13	100.34	PASS
TSS	11/29/2012	4030	WP-214	80.6	81.5	66.6-90.7	98.9	PASS
Si	11/29/2012	785	SI80-785	26.57	27.9	23.7-32.1	95.23	PASS
BOD	12/17/2012	578	WP-214	207.4	112	56.9-168	185.18	FAIL
CBOD	12/17/2012	578	WP-214	154.2	96.8	43.4-150	159.3	FAIL
TOC	11/29/2012	578	WP-214	80	72	60.2-82.8	111.11	PASS
BOD	1/30/2013	516	P209-516	50.81	49.4	24.7-74.0	102.85	PASS
CBOD	1/30/2013	516	P209-516	40.85	42.5	19.0-66.0	96.12	PASS

^aEERP's QA requirements for standards to pass is $\pm 20\%$ of the expected value so TP was considered passing even though it was outside of the acceptance limits set by ERA.

Figure 1. Comparison of filtering phosphate samples within 15 minutes of collection in the field and analyzing within 2 days to filtering within 24 hours in the laboratory and analyzing within 28 days.

